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M.I. Aranguren, E. Mora, C.W. Macosko

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Small deformation tests were done using oscillatory shear and showed coupling of the filler and crosslinking effects at high crosslinking density while the effects are more or less independent at low crosslinking levels.

As in the case of uncured composites, the moduli of the samples increase with silica concentration and amount of silanols on the silica. Low PDMS gives higher modulus, more brittle rubbers than those obtained from high molecular weight PDMS. Since the crosslinking (hydrosilation) proceeds through the end vinyl groups of PDMS, lower molecular weight polymers obtain higher crosslinking densities.

A silica treated with divinyltetramethyldisilanzane gave products with moduli similar to those obtained from untreated silicas. This highlights the importance of good adhesion of filler to polymer to obtain materials of high modulus.

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RHEOLOGY OF FILLED RUBBER:
SILICA-SILICONE

Mirta I. Aranguren[†], Elsi Mora, Christopher W. Macosko*

Department of Chemical Engineering and Materials Science, University of Minnesota

Abstract

This work focuses on the relationship between the morphology of filled rubber and its behavior at small and large deformations. Composites made from vinyl terminated polydimethylsiloxane and different fumed silicas were prepared. Filler concentration ranged from 0 to 40 phr (parts of silica per hundred parts of PDMS).

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* to whom correspondence should be addressed

† M. Aranguren is a member of the Consejo Nacional de Investigaciones Cientíaficas y Técnicas (Argentina)

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SILICA-SILICONE

Mirta I. Aranguren[†], Elsi Mora, Christopher W. Macosko
Department of Chemical Engineering and Materials Science, University of Minnesota

Introduction

Commercial applications of elastomers require the use of solid fillers to obtain the desired reinforcement. Although these systems have been used for many years, the mechanism of reinforcement is still not well understood. Important contributions to the area have been made in the past by Smallwood [1], Guth [2], Medalia [3], Mooney [4], and many others. However, due to the complexity of the system, a general model that is successful in representing the behavior of the rubber under different tests has not been developed. Complexities come from the polydispersity of the initial chains, the distribution of the aggregate sizes, and the fractal characteristics of the fillers. This results in the filler effective volume being much larger than what can be calculated from its weight. This also affects the reactivity of the filler surface towards the polymer.

Instead of trying to find a phenomenological model that could explain only one test, the goal is to understand the relation between the morphology of the rubber and its rheological behavior. From there, a mathematical formulation could be produced. This model will probably be more complex than the phenomenological approach, but hopefully it will be more general.

Silica-silicone rubber was used as an example of particulate filler reinforcement of elastomers. In an earlier paper we studied the adhesion of polydimethylsiloxane (PDMS)-silica and how it changes with PDMS molecular weight and silica surface treatment [6]. The results showed that the amount of polymer adsorbed per unit mass of silica is more or less independent of the silica concentration at concentrations ≤ 8.1 volume %, and increases with the concentration of silanols on the silica surface and with the PDMS molecular weight. Then, we studied the rheology of uncured silica-PDMS suspensions.

† M. Aranguren is a member of the Consejo Nacional de Investigaciones Científicas y Técnicas (Argentina).

The importance of the filler-polymer attachments in the reinforcement and relaxation behavior of these materials was stressed. It was evident that suspensions prepared from PDMS of molecular weights $M_w \leq M_{en}$ (critical molecular weight for entanglements) behaved differently from suspensions made from high molecular weight PDMS [10, 18].

In this paper, experimental results of dynamic and tensile tests on cured filled silicone rubbers are presented. The variables studied are: silica concentration, silica surface treatment, and the crosslinking density of the matrix. As in the two previous papers the effect of the filler structure was not analized. All the silicas used came from the same untreated silica in order to minimize structual differences of the aggregates.

The physical picture from the results of the previous two papers is one in which aggregates are primarily connected through different types of intermediate linking PDMS chains. The same picture is valid here, but the crosslinking reaction reduces the importance of entanglements or "bridging" chains. Thus, similar trends are seen in the behavior of cured and uncured materials, but stronger in the uncured suspensions.

Materials

Vinyl terminated polydimethylsiloxanes of polydispersity (M_w/M_n) about 2 were used in this study. The polymers and crosslinker were supplied by Dow Corning (Midland, MI), except for PDMS1, which was bought from Petrarch. The materials characterization is presented in Table 1.

The crosslinking reaction is hydrosilation, shown below. The value of M_n/f (f= average functionality of the molecule) for the crosslinker is 134.5 and was determined by using a method of mercury (II) reduction [5]. The ratio of SiH to C=C was kept equal to 1.8 in most of the samples to compensate for SiH groups consumed in secondary reactions and thus, to obtain complete conversion of the vinyl groups. The catalyst used was a salt of Pt(II), Dow Corning plant grade. An inhibitor was also used to avoid reaction during mixing and loading of the sample in the rheometer or filling of the tensile mold.

$$\equiv SiH + -CH=CH_2 \xrightarrow{\text{Pt (II)}} \equiv Si\text{-}CH_2\text{-}CH_2\text{-} \qquad (1)$$
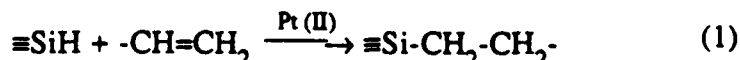
Fumed silicas of similar structure and surface area were used in the study. We used an untreated fumed silica (Aerosil 130, Degussa) and different modifications of it [6]. The main characteristics of these silicas are summarized in Table 2. The silica surface treatments were obtained by reacting Aerosil 130 under mild conditions with disilazanes

[6,9], except for Aerosil R972 which is a commercial product obtained from the reaction of Aerosil 130 with dichloromethanes.

Compounding

The materials were compounded at room temperature in a Haake Rheomix 600 with a chamber capacity of 60-70 cm^3 using sigma blades at 35 rpm. The master batch (40 phr, parts of silica per hundred parts of polymer) made from Aerosil R972 and PDMS4 was the only one prepared in a Baker Perkins mixer of 1ℓ of capacity (Midland) using helical rollers (35 rpm) and then diluted down in a kitchen mixer to prepare less concentrated suspensions. The procedure followed for mixing was the same for all the materials and the total time since silica addition until unloading of the filled melt was three hours [6]. No additives were used in the compounding.

Oscillatory Shear Measurements

Experimental

The crosslinker, catalyst and inhibitor were added to the suspension PDMS-silica and mixed with a spatula in a watch glass, spreading it thin at the end of the mixing to facilitate the elimination of bubbles. Then, we loaded the sample in the rheometer, we used a Rheometrics System IV in its dynamic shear mode with geometry of parallel plates.

The material was loaded onto the lower plate, so the sample was thicker in the center of the plate than at its borders. In this way, when the lower plate is lifted, the first contact of the sample with the upper plate is in the center minimizing the possible trapping of an air layer between sample and plate. Many samples required the use of sand blasted plates to avoid slippage during the test. After loading, the environmental chamber was closed around the plates and the reaction carried out at 150°C for about 1 hour under N$_2$ purge. No measurements were done during curing.

Recovery of the Cured Samples

Samples deformed up to about 20 % shear strain showed complete recovery. The crosslinking points give the sample enough cohesion not to develop cracks on the edges which was seen to happen in the uncured materials [10]. Larger deformations were obtained only in tensile tests, since in the shear tests, large deformations usually led to slippage from the plate if the surface of the plates was smooth or tended to exceed the transducer limit aborting the experiment.

Results

The samples studied include filled and unfilled cured materials. The results reported here were obtained at temperatures between 26°C and 30°C unless otherwise indicated.

Cured Samples

<u>Pure PDMS:</u> Since the crosslinking reaction is by end-linking, the lower the initial molecular weight of the polymer the higher the modulus of the cured material. Thus, moduli for PDMS2 and PDMS3 were 1.45×10^5 Pa and 2.1×10^5 Pa respectively. The frequency sweep showed that the modulus is independent of the frequency, as expected in a fully reacted material. The low value of these moduli could be due to a significant concentration of pendant chains. Because the average functionality of the polymers was found to be lower than 2 (f= 1.7 and 1.4 for PDMS2 and PDMS3 respectively), even when nominally they were vinyl terminated.

<u>Composites</u>

Effect of the Silica Concentration: By increasing the silica concentration the modulus of the material is increased. Figure 1 shows this effect for two composites made from PDMS4 and Aerosil R972 with silica concentrations of 20 and 40 phr which correspond to 8 and 15% by volume. However, the relative increase in G' is not as strong in the cured rubbers as it was in the uncured state [10].

Effect of the PDMS Molecular Weight: Changing the initial molecular weight of the polymer has the same effect observed in unfilled materials. The lower the initial molecular weight of the PDMS, the higher the modulus of the cured rubber (3.2×10^5 Pa and 5.9×10^5 Pa for PDMS2+MS1(20 phr) and PDMS3+MS1(20 phr), respectively).

Effect of the Silica Surface Chemistry: As it occurs with the uncured rubbers, the higher the OH concentration on the silica surface the higher the modulus. The ratio between the moduli of the cured PDMS4+A130 (20 phr) to PDMS4+MS1 (20 phr) is 1.6 in the LVE region (7×10^5 Pa and 4.5×10^5 Pa respectively), while for the uncured rubbers this ratio is about 300 (3×10^5 Pa and 10^3 Pa [10]). Both moduli were measured at 50 rad/s. Thus, this large difference is lost during curing. These composites are usually processed with a partially treated silica, so that the viscosity of the uncured material is not too high and still a final product of high modulus can be obtained. The completely treated silica gives a rubber

of low modulus and this is probably related to the poor adhesion of the polymer onto the filler, the bound rubber is approximately zero for these composites [6].

Effect of the Degree of Crosslinking: We studied the effect of different levels of crosslinking on the rheology of the samples. PDMS4+R972 (20 phr) was reacted with different amounts of crosslinker, so that the ratio of silane to vinyl groups was SiH/SiC=C = 1.8, 0.9, 0.45, 0.225, and 0.

Figure 2.a shows the results obtained for G' vs % strain (linear scale for G'). The figure shows the curve for a the completely cured sample (SiH/SiC=C = 1.8) and other two lower levels of crosslinker (not enough SiH groups to completely cured the sample). The overall effect of the crosslinking density is large at this molecular weight. The results obtained at low crosslinking levels are shown separately in Figure 2.b. The filler presence makes difficult to determine the critical ratio SiH/C=C at which gelation occurs. The test in the unfilled material gave a ratio of 0.27, thus as an approximation the sample at SiH/C=C = 0.45 was chemically gelled and the one at 0.225 was not. The curves look almost parallel, but at large strains the crosslinked samples broke or slipped from the plates.

Tensile Tests

Experimental

The samples were cured with an excess of crosslinker (SiH/C=C = 1.8), the same excess used in the crosslinking of the samples tested dynamically (previous section). This excess was used to completely react the vinyl groups, since the crosslinker participates in secondary reactions that may lead to the loss of volatile reactive molecules [11,12] and others such as the reaction with the "inhibitor" (retarder) and a possible minor reaction with the available silanols on the silica filler. All the samples were prepared maintaining the same proportion of SiH/C=C groups, including the samples containing silica with vinyls where an estimation of the number of attached vinyls was done (assuming that all the free silanols reacted, 1.8 OH/nm^2, [13]) and the corresponding excess of crosslinker was added.

Apparatus:

Most of the samples were tested using an Instron 1122 in Dow Corning, Midland. Neumatically closing grips with serrated faces were used to keep the sample from slipping

and an extensometer (XL Balanced Elastomeric Extensometer, Instron) was used to measure the sample elongation. Three more samples were tested in our laboratory using an Instron 1011. The time and crosshead speed were used to calculate the elongation at any given time. We used screw action grips with serrated faces in these tests. The rate of elongation in both cases was 50 cm/ min [14], however some samples were also run at lower crosshead speeds. All the tests were done at room temperature.

Specimen preparation:

Individual molds were used for each specimen because enough material was not available to produce large slabs. This, of course, leads to some problems. The edges of the mold usually concentrate stresses and some tearing may occur on the borders of the samples during demolding. For these reasons, the failure behavior of the samples was not quantitatively studied.

During mixing of the polymer with the crosslinker many air bubbles are trapped in the sample. The formulation includes an inhibitor that is much more reactive than the vinyls with respect to the crosslinker, so that the material can be molded before it reacts. The reactive mixture is put in an open mold where the air bubbles slowly move up towards the free surface. No vacuum was used in order to avoid the evaporation of the inhibitor and the acceleration of the reaction. After that, the excess material was removed with a razor blade and the mold was closed. The samples were cured at 150°C with a slow purge of nitrogen. The final specimens had no bubbles at all or just a few small bubbles, samples showing large bubbles (1-2mm diameter) were rejected.

Thicker specimens have to be prepared for the samples made of unfilled rubber since regular size specimens required forces too small to be measured accurately with the piece of equipment used. These rubbers are very soft but brittle. They had to be put between the grips with great care, because they were so fragile that some broke during that process (catastrophic failure that leaves crumbs of rubber).

The dog-bone specimens (central section: 50 x 7.94 x 3.18 mm) had dimensions close to those obtained using a die A [14] except for the unfilled specimens (double thickness).

Results

Effect of the Silica Concentration: In spite of the problems discussed with respect to the rupture of the materials, the relative trends seem to be still valid. Figure 3 shows the behavior of the unfilled rubber (PDMS4) and the composites made with Aerosil R972 at

two different concentrations. The composite with 10 phr of silica shows improvement with respect to the unfilled sample, the Young's modulus is 24 % larger for the filled sample which also breaks at larger elongations. The composite with 20 phr of silica has a Young's modulus 110 % larger than the unfilled material and it breaks at an elongation a 40% larger. In general the addition of silica to the rubbers improves the modulus and shifts the fracture to larger elongations. Table 3 shows this effect in composites prepared from PDMS2 PDMS3 and PDMS4.

The results of moduli reported in Table 3 are the average of three to six runs for each material, except in the case of PDMS3+MS2 (20 phr) which is the result of only one sample. Due to the uncertainty of the fracture data they are not averaged and the range of values observed is reported. The Young's moduli are comparable to those reported by Maxson and Lee for similar systems [9].

Effect of the Silica Surface Chemistry: Figure 4 shows the results obtained from composites prepared from PDMS2 and silicas with different surface treatments. In general, Aerosil R972 gives composites with better properties than Modified Silicas 1 and 2. Modified Silica 2 (low vinyl concentration) gives rubbers which have essentially the same behavior than Modified Silica 1 (methyl groups); actually, Figure 4 shows even a slightly lower curve for the first composite than for the latter. It was thought that perhaps the vinyl concentration was too low to notice any difference and thus, another sample was prepared with a silica modified with a larger amount of vinyls (Modified Silica 3). The measurements on this sample were done in our laboratory and showed an important improvement on the properties of the final product (Figure 4 and Table 3). Figure 5 shows a comparison between composites prepared from PDMS3 with Modified Silica 3 and unmodified fumed silica (Aerosil 130). The moduli are similar but the former breaks at larger elongations than the latter.

Effect of the initial PDMS Molecular Weight: Other point of interest to consider is the effect of different molecular weight PDMS matrices. Figure 6.a. shows the behavior of composites made from Modified Silica 2 (low vinyl concentration) with PDMS2 and PDMS3. The low molecular weight polymer gives a material of high modulus that breaks at smaller elongations. The high molecular weight PDMS gives larger elongation at fracture (comparative values). Figure 6.b shows a similar behavior of the composites made from methylated silica with PDMS2 and PDMS4.

Hysteresis: We studied the hysteresis of the materials using some of the samples. They were deformed up to 50-100% elongation (depending on the material) and then they were allowed to rest at room temperature in the unstressed state for 40 hours. After that period, they were tested again, but there was no measurable recovery.

Rate of extension: PDMS2+ MS3 (20 phr), PDMS3+ MS3 (20 phr) and PDMS3+ A130 (20 phr) were run at different rates of elongations. The results superposed almost exactly, that is, the crosshead speed did not affect the results up to elongations close to fracture (60-120% depending on the material).

Discussion

Model: Physical Picture

The experimental results can be explained using the same model proposed for the uncured materials in a previous paper [10]. In that case, bound rubber, FTIR and rheological results could all be explained by a model where the silica surface is surrounded by a shell of adsorbed polymer and the agglomeration (clustering of the aggregates) took place through the intermediate polymer chains.

Different types of filler-polymer-filler linkages are possible. Figure 7 shows a schematic diagram (not at scale) of the linkages:

    a) direct bridging, a chain is adsorbed to two different aggregates,

    b) bridging due to the entanglement of two chains adsorbed to two different

    aggregates,

    c) bridging due to entanglements of free chains.

All of these types of linkages will be effective in increasing the modulus of the composite, however the types (a) and (b) will also change the qualitative behavior of the uncured rubbers. Because adsorbed chains have reduced mobility their maximum relaxation time is larger than that of a bulk (non-adsorbed) chain. Thus, the life time of bridges of type (a) and (b) is larger than that of bridges of type (c). These features change the response of the material at long times in a stress relaxation test or at low frequencies in dynamic tests.

After reaction (Figure 8) the linkages become all very similar since:

    a) due to chain-chain crosslinking (hydrosilation), all the aggregates become attached

    to one another through the reacted polymeric matrix,

b) some reaction may take place between the silica silanols (if they are present) and the adsorbed polymer [10, 17], which improves the adhesion filler-polymer.

The results obtained for the cured samples in dynamic shear showed that :

1) The completely reacted system becomes frequency independent.

2) The storage modulus increases with silica concentration and crosslinking density (vinyl terminated PDMS of decreasing molecular weight). The effect of the silica concentration is still very important but less dramatic than in the uncured material.

3) The larger the OH concentration on the silica surface, the larger the modulus, but again the effect in the rubbers is less dramatic than for the uncured materials. No appreciable difference was found between composites made of Modified Silica 1 and Modified Silica 2. However, the effect of a larger concentration of surface vinyls was found to affect the tensile response of the rubbers.

4) The most important conclusion from the results obtained for crosslinked materials is that, in general, the effect of the structure (agglomeration) is dependent on the crosslinking density of the rubber. This additional complexity appears due to the filler-polymer-filler linkages and it can be neglected only when the crosslinking density is low (Figures 2.a and b).

The effects of silica concentration and and surface OH are the same seen in the study of the uncured materials [10], but they are less intense in the cured rubbers, because in this case the matrix is joining every aggregate and thus the results are not so much dependent onentanglements or bridging. Chahal and St Pierre [15] also noticed that after curing the properties of the materials are less dependent on the silica surface chemistry than in the uncured state.

The effect of the PDMS molecular weight is better discussed in terms of the crosslinking density, which is addressed in more detail below.

Effect of the Crosslinking Density: It is important to first review the results of Payne et al [16] working with natural rubber and carbon black. They showed that in a linear scale the G' vs strainwork (stress*strain) curves for the unvulcanized and vulcanized rubbers were almost parallel, that is the only effect of the chemical crosslinking was to shift up the curve of the modulus for the unvulcanized rubber. Based on these results the authors concluded that the effect of the agglomeration of the carbon black is independent of the crosslinking level of the polymeric matrix. Thus, these contributions to the modulus are additive, can be studied separately and added later to predict the behavior of the vulcanized rubber. These

results have been used by many researchers to deduce that agglomeration is due exclusively to filler-filler interactions and it is independent of the matrix.

The results that we obtained for different levels of crosslinker were presented in the Figures 2.a and b. The effect of the filler structure is essentially the same at low density of crosslinking, just as observed in Payne's work. At high levels of crosslinking the agglomeration effect increases with increasing crosslinking density. In these conditions, the two effects (crosslinking and structure) rather than additive are interactive and cannot be separated. Two possible reasons to explain the differences between the silicone and the natural rubber results are:

1) the agglomeration in the natural rubber-carbon black systems is mainly due to filler-filler interactions (as suggested in the literature), or

2) the crosslinking density is low in that system.

The second has the advantage of being able to explain both results. The long natural rubber chains are vulcanized by only a few points of crosslinking along the chain (long segments between crosslinking points), which means only a small change in the matrix. In our system, complete crosslinking means a high density of crosslinking (shorter chains) and a big change in the polymer matrix which means a big change in the linkage between the aggregates. The overall shift due to the reaction, even without considering the agglomeration effect, is relatively much bigger in the case of the silicone rubbers than in the case of carbon black-natural rubber. $G'_{(\gamma \to \infty)}$ changed from 0.42 MPa for the unvulcanized carbon filled NR to 0.88 MPa for the vulcanizate, while in the silica-silicone case, $G'_{(\gamma \to \infty)}$ changed from 1.4×10^{-4} MPa when uncured to 0.35 MPa after cure.

Tensile tests

Silica Concentration: Composites show improved modulus and fracture behavior than the unfilled rubbers. The increment in modulus is the expected reinforcement effect, the improvement in the failure properties is not so simplisticly explained. Usually, an increased stiffness of a sample goes associated with a smaller elongation at fracture. However, the fracture of an elastomer is through propagation of a crack and the presence of a filler can disturb the path of a crack or stop it completely so that the fracture is shifted to larger elongations. Thus, for these soft but brittle silicone elastomers the benefits of adding fillers are multiple.

Silica Surface Chemistry: Table 6 does not show very well the differences between the results obtained for the composites prepared with Aerosil R972 (low concentration of

surface free OH) and those made from Modified Silicas 1 and 2 (no surface free OH). The differences are shown more clearly in the Figure 4. and appear at medium and large deformations. The modulus of the composite made from Aerosil R972 is higher than that of the sample made from Modified Silica 1.

The results obtained using a silica with a high vinyl concentration (Figure 4) are even more interesting when comparing the modulus of the uncured materials (Figure 9) obtained by dynamic measurements. The modulus of PDMS2+MS3 (20 phr) is 2.5 times larger than that of PDMS2+MS2 (20 phr) which was not expected and may be due to some differences in the dispersion of the filler. More importantly the modulus of PDMS2+MS3 (20 phr) is lower than that of PDMS2+R972 (20 phr) when uncured, but the situation is reversed after curing. This means that one could process a material about six times less viscous than PDMS2+R972 (20 phr) to obtain a product of twice its modulus. This observation was previously reported by Maxson and Lee [9] who used a similar treatment for the fumed silicas. The improvement in the modulus of the composites was also dramatic in their study. Unfortunately, they did not characterize the silicas after treatment, but in view of our own results we think that they must have obtained the same type of increased silica-polymer attachments that we did.

Of course the reaction of the silica surface means that the crosslinking density is larger in PDMS2+MS3 (20 phr) than it is in PDMS2+R972 (20 phr), but let us consider the location of those crosslinks. These extra bonds do not happen in the bulk of the matrix (thus, increasing the modulus of that phase), but in the interface silica-rubber (thus, improving the adhesion polymer-filler). The case should be similar to that of an untreated silica where the surface silanols react with the polymer [17] and thus, the modulus should be similar in both cases. That comparison was shown in Figure 5 for PDMS3+MS3 (20 phr) and PDMS3+A130 (20 phr). The two curves look very similar, except that PDMS3+A130 (20 phr) breaks at smaller elongations, but more measurements are needed to verify this trend in failure. In any case, it could be explained by the type of reactions that take place in the silica polymer interface. If the silica is untreated the OH react by cleavage of the PDMS chains and further reaction of the resulting OH terminated PDMS with another surface OH [17]. In the case of Modified Silica 3 the surface vinyls react with the crosslinker that also reacts with the PDMS vinyl terminated chains forming a covalent filler-polymer linkage. This second process does not break chains, that is, it does not reduce the chain length between crosslinks and thus, it generates more flexible links.

PDMS Molecular Weight: As already seen in the presentation of the dynamic shear results, the lower the molecular weight, the higher the crosslinking density and thus, the higher the modulus. Also the more brittle the resulting rubber which breaks at smaller deformations as illustrated in Figures 6.a and b.

Comparison to the results obtained from dynamic shear: From the results of tensile tests we calculated the modulus predicted by the rubber elasticity theory in order to quantify the differences between the samples.

The rubber elasticity theory predicts that the relation between the tensile stress and the elongation ratio, λ, is:

$$\sigma = G \left(\lambda - \frac{1}{\lambda^2} \right) \qquad (2)$$

where: σ is calculated as force/initial cross-section area of the specimen, G is the rubber elasticity modulus and λ is L/L_0, with L being the distance between two points in the tensile specimen at any time and L_0 being L at time=0.

Figure 10. shows the fitting of the results to equation (2). The correlation factor was 0.99 or better in all the tests. The values of G obtained from the tensile results were compared to the equilibrium modulus $G'_{(\gamma \to 0)}$ of the cured samples measured by dynamic shear tests. Table 4 shows that comparison, the agreement between the two sets of data is good for most of the samples.

G. Summary and Conclusions

We have presented the effect of the filler concentration, surface treatment and the effect of the density of crosslinking on the rheological behavior of the cured rubber. The study was complemented with tensile tests of the fully cured samples to obtain information about their response at large deformations. A summary of the experimental observations is included below:

1. Crosslinking density:

At high crosslinking levels the contribution of agglomeration increases with increased crosslinking density. This indicates that these contributions are not additive as frequently suggested in the literature.

13

The low molecular weight PDMS rubbers have higher modulus, but are more brittle than the high molecular weight PDMS rubbers due to higher crosslinking density.

2. Silica Concentration:

Addition of filler to rubber improves its final properties: modulus and fracture behavior. This last improvement occurs because the filler acts as a crack stopper or just changes the path of a crack so that failure is delayed.

3. Silica Surface Chemistry:

The composites made from untreated silicas show higher moduli but they are also more brittle. Test of composites prepared with Modified Silica 3 (high vinyl concentration) yielded additional information. These composites show a modulus comparable to that obtained with untreated silicas and have the advantage they have low viscosity during processing.

4. Hysteresis:

It was observed after elongations ≥ 50% that it was an irreversible phenomenon at least at room temperature, even after 40 hour at rest.

5. Rubber Elasticity:

The rubber elasticity equation fits the experimental data quite well up to extensions of 60 to 120% (depending on the samples) and the modulus obtained is in reasonable agreement with $G'(\gamma \rightarrow 0)$ obtained by dynamic measurements.

Note: The limitations of the tensile results with respect to a quantitative study of the fracture behavior were indicated.

A physical model was proposed that takes into account these observations. A diagram including the different types of possible filler-polymer-filler linkages was presented (Figures 7, 8). The main idea proposed is that the forces exerted between aggregates are mainly due to the polymer bonding. This model can explain the larger amount of bound rubber in untreated silicas [6], the change in the relaxation spectrum of the uncured material [10], the non-additivity of the agglomeration, and crosslinking density effects.

The same trends observed for uncured materials (except for the molecular weight dependence) hold for the rubbers, but the effects of the filler are less intense, because the entanglement and bridging processes are not as important on the rheology of cured rubbers. However, the intermediate polymer chains that contribute to agglomeration in the uncured state still play a role in the non-additivity of the crosslinking density and the reinforcement effects. Obtaining high modulus materials by adding silicas with reactive surfaces can be

traced back to the number of reaction sites on the silica surface and the increased strength of the filler-polymer interface.

Acknowledgements

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Table 1

Molecular Weights and Polydispersity of the Polydimethylsiloxanes

	M_n	M_w	M_w/M_n
PDMS1[a]	146,000	325,000	2.2
PDMS2[b]	66,400	118,000	1.8
PDMS3[b]	8,900	16,500	1.9
PDMS4[c]	22,600	87,600	3.9
Crosslinker[a]	537	786	1.5

a. Measured in our laboratories, Waters GPC model 150-C ALC/GPC (1% solution in THF).

b. These values were obtained using a PDMS calibration by the Dow Corning laboratories (Midland).

c. A mixture of PDMS2 and PDMS3, 70:30 wt % respectively.

Table 2

Characterization of the Fumed Silicas

Note: The base product for all the treated silicas was Aerosil 130.

	BET surface (m^2/g)[a]	% hydroxyl treated [b]	Type of treatment
Aerosil 130 (A130)	133	0	None
Aerosil R972 (R972)	108	10 (30[c])	Dimethyldichlorosilane
Modified Silica 1 (MS1)	112	100	Hexamethyldisilazane
Modified Silica 2 (MS2)	114	100	Divinyltetramethyldisilazane (67wt%) + hexamethyldisilazanedisilazane (33wt%)
Modified Silica 3 (MS3)		100	Divinyltetramethyldisilazane

a. Measured by Micromeritics, Inc.
b. Measured by methyl red adsorption [7].
c. From Degussa catalog [8].

Table 3

Tensile Results (rate of elongation= 500 mm/min)

Sample	E(MPa)	G(MPa)	% ε_b	σ_b(MPa)
PDMS2	0.56	0.18	97-105	0.28-0.29
PDMS2+MS1 (20 phr)	1.1	0.38	240-311	1.38-1.75
PDMS2+MS2 (20 phr)	0.91	0.32	235-246	1.33-1.29
PDMS2+R972 (20 phr)	1.05	0.35	199-256	1.33-1.79
PDMS2+MS3 (20 phr)	2.08	0.71	169-268	1.43-2.6
PDMS3+MS2 (20 phr)	2.45	0.76	53	1.31
PDMS3+MS3 (20 phr)	3.01	1.0	68-74	1.27-1.49
PDMS3+A130 (20 phr)	3.18	1.1	35-43	0.74-0.93
PDMS4	0.58	0.18	51-113	0.2-0.31
PDMS4+MS1 (20 phr)	1.4	0.43	150-210	1.13-2.07
PDMS4+R972 (20 phr)	1.22	0.47	140-160	1.29-1.69
PDMS4+R972 (10 phr)	0.72	0.32	110-148	0.58-0.81

% ε_b is the percentage of elongation at fracture ($\Delta L/L_o$ *100).

σ_b is the engineering stress at fracture (F/A_o).

Cured PDMS3 breaks under the pressure of the grips and it could not be tested

Table 4

Comparison of the rubber elasticity modulus and $G'_{(\gamma \to 0)}$

Sample	$G_{rubber\ elast.}$(MPa) $(\lambda \to 1)$	G'(MPa) $(\gamma \to 0)$
PDMS2	0.18	0.15
PDMS2+MS1 (20 phr)	0.38	0.33
PDMS2+MS2 (20 phr)	0.32	0.21
PDMS2+R972 (20 phr)	0.35	0.39
PDMS3	**	0.21
PDMS3+MS2 (20 phr)	0.76	0.59
PDMS4	0.18	0.19
PDMS4+MS1 (20 phr)	0.43	0.44
PDMS4+R972 (20 phr)	0.47	0.40

** It breaks under the pressure of the grips long before the tensile test is begun.

Figure 1. Cured Samples: Strain sweep of filled polydimethylsiloxanes (ω=50 rad/s). Open symbols correspond to 20 phr, filled symbols correspond to the results for 40 phr.

Figure 2.a. Cured Samples: Strain sweep of the composites prepared from PDMS4 and Aerosil R972 (20 phr) at different crosslinker levels. All the samples were gelled.

Figure 2.b. Cured Samples: Strain sweep of the composites prepared from PDMS4 and Aerosil R972 (20 phr) at different crosslinker levels. Only the upper curve represents a gelled sample, the lowest one corresponds to the uncured sample and it is included for comparison.

Figure 3. Tensile results for the cured PDMS4 and the rubbers prepared from PDMS4 and Aerosil R972 at two different concentrations.

Figure 4. Composites prepared from PDMS2 and fumed silicas with different surface treatment. All composites contain 20 phr of silica (8 % vol.).

Figure 5. Composites prepared from PDMS3. PDMS3+MS2 (20 phr) is included just to complete information and for comparison with the other two more reinforcing silicas.

Figure 6.a. Composites prepared from Modified Silica 2 (20 phr) with PDMS2 and PDMS3.

Figure 6.b. Composites prepared from Modified Silica 1 (20 phr) with PDMS2 and PDMS4.

Figure 7. Schematic diagram of the different types of contact filler-polymer-filler that would lead to agglomeration of individual aggregates. Each groups of particles in the diagram represents an aggregate (primary structure in the rubber). The drawing is not done at scale. The number of particles per aggregate is much larger than what it is shown here. a) Direct bridging, b) bridging by entanglement of adsorbed chains, c) bridging by entanglement of non adsorbed chains.

Figure 8. Schematic diagram of the rubber before and after the crosslinking reaction. Open circles represent sites where the polymer has reacted with the filler; filled rectangles represent polymer-polymer crosslinking points.

Figure 9. Strain sweep of three uncured composites made from PDMS2 and different treated silicas.

Figure 10. Fitting of experimental data to the rubber elasticity equation to find the modulus of the sample. The results from two specimens made with Modified Silica 1+PDMS4 (20 phr) are shown.
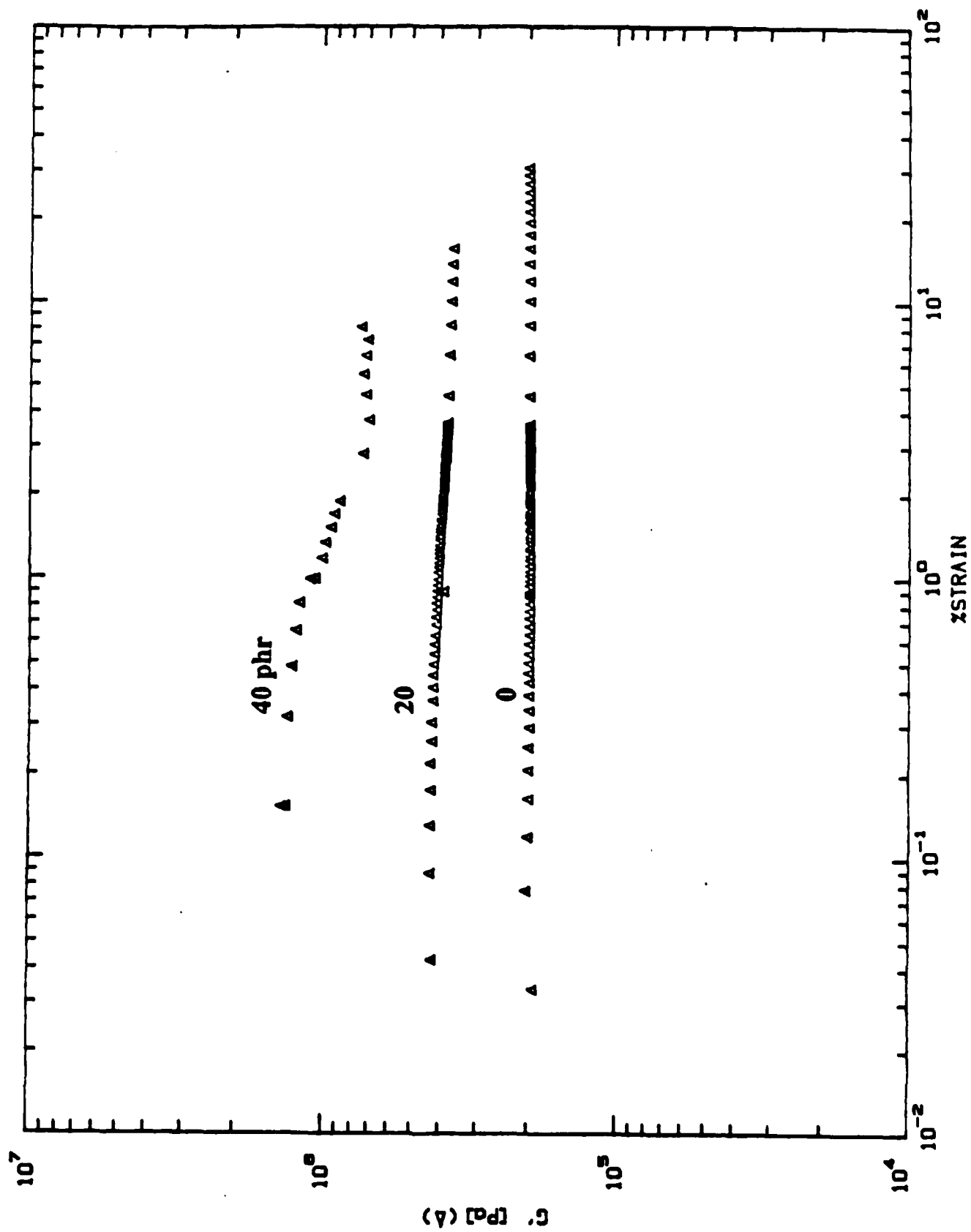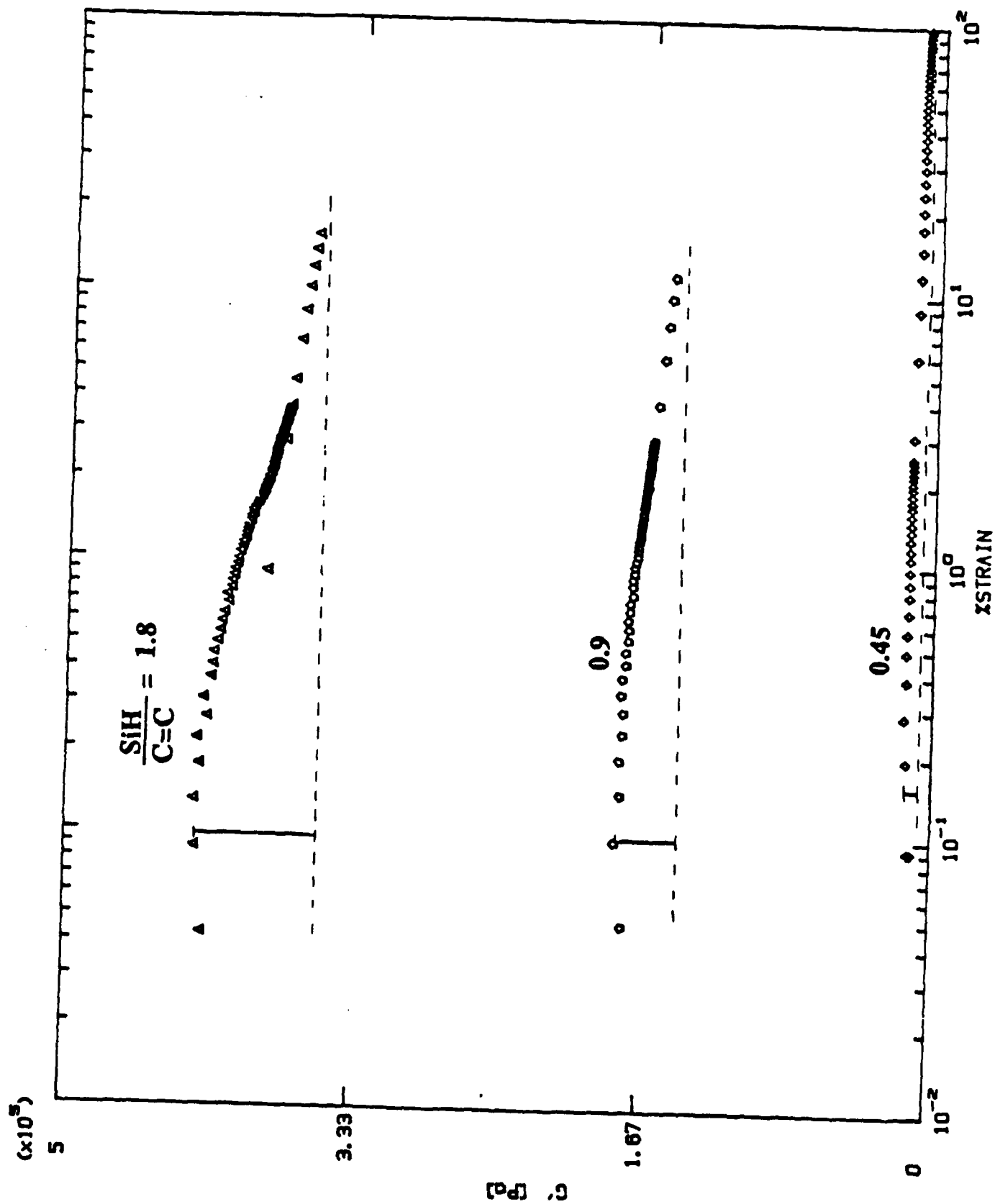
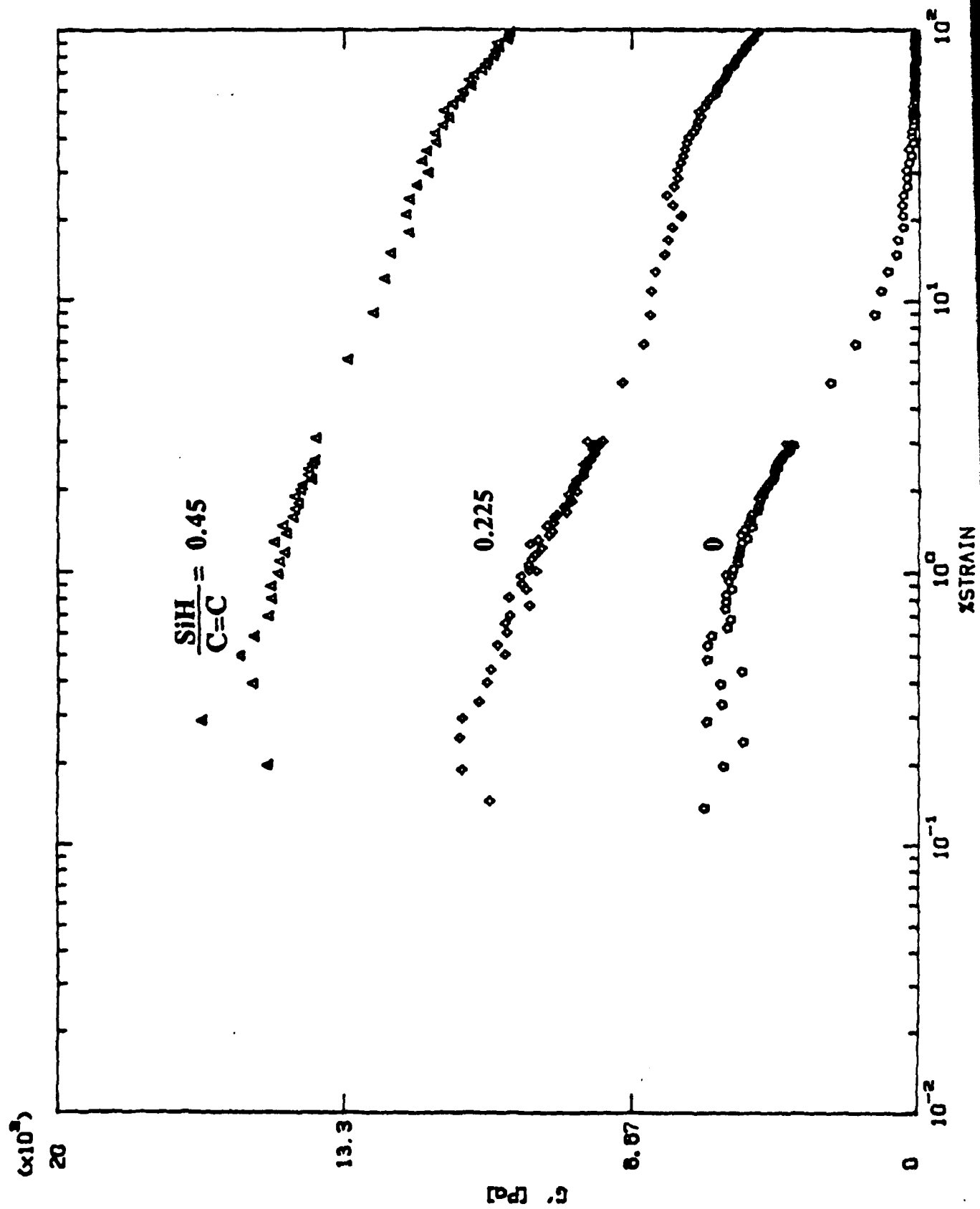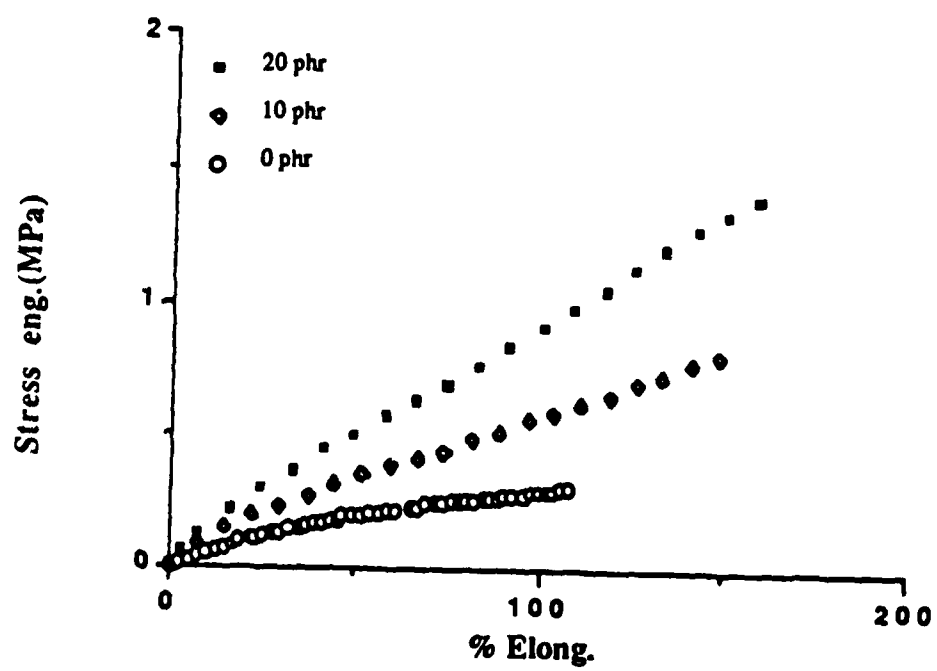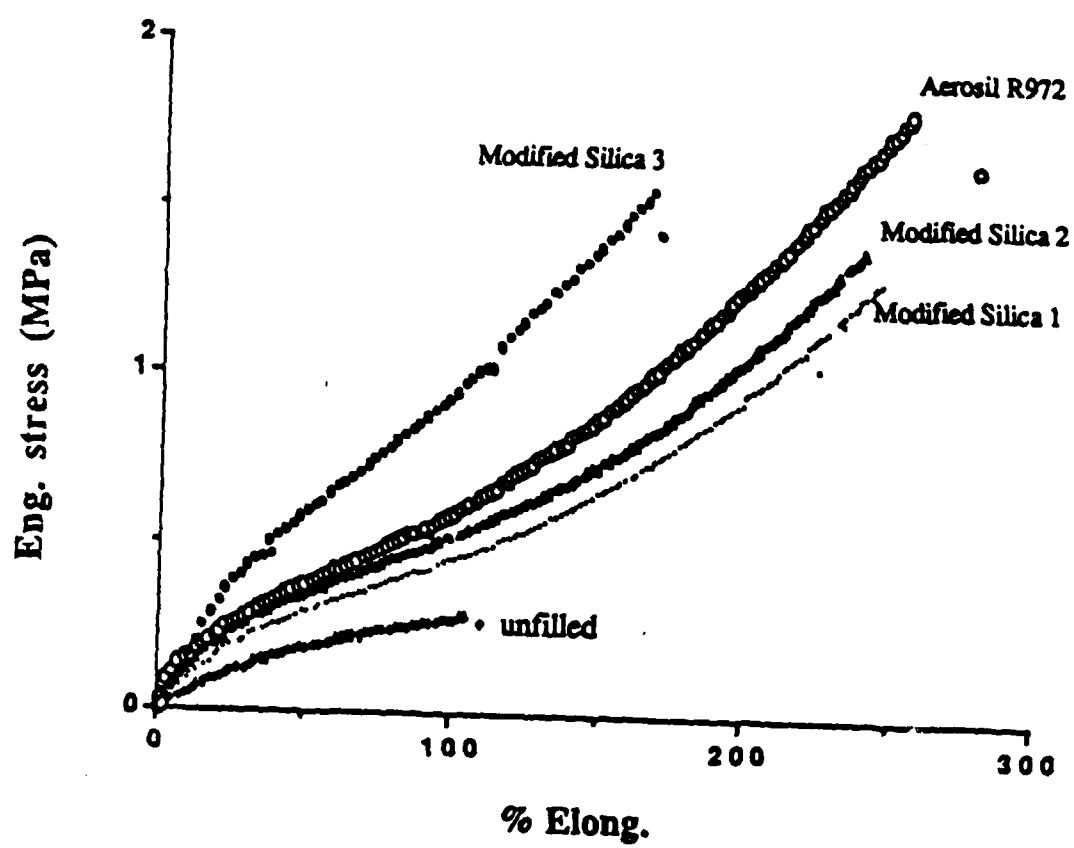Figure 1

Figure 2.a

Figure 2.b.

Figure 3.

Figure 4

Eng. stress (MPa) vs % Elong.

Curves labeled: Aerosil R972, Modified Silica 3, Modified Silica 2, Modified Silica 1, unfilled
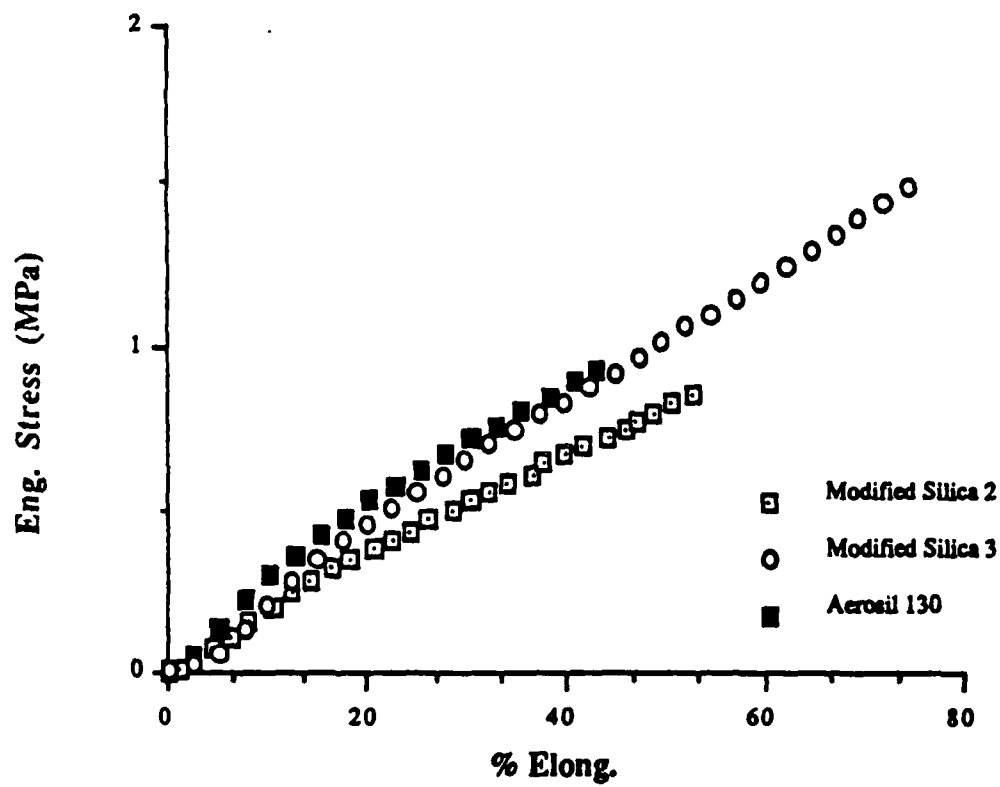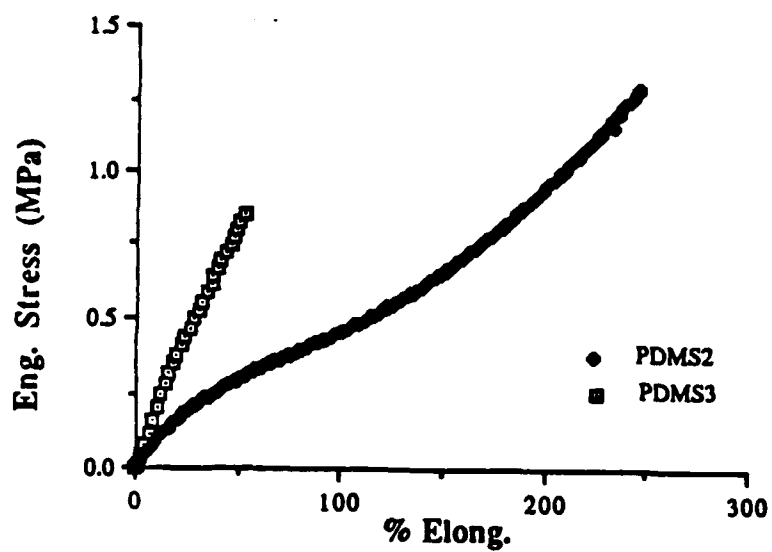
Figure 5

Figure 6.a.

Figure 6.b.

Figure 7.

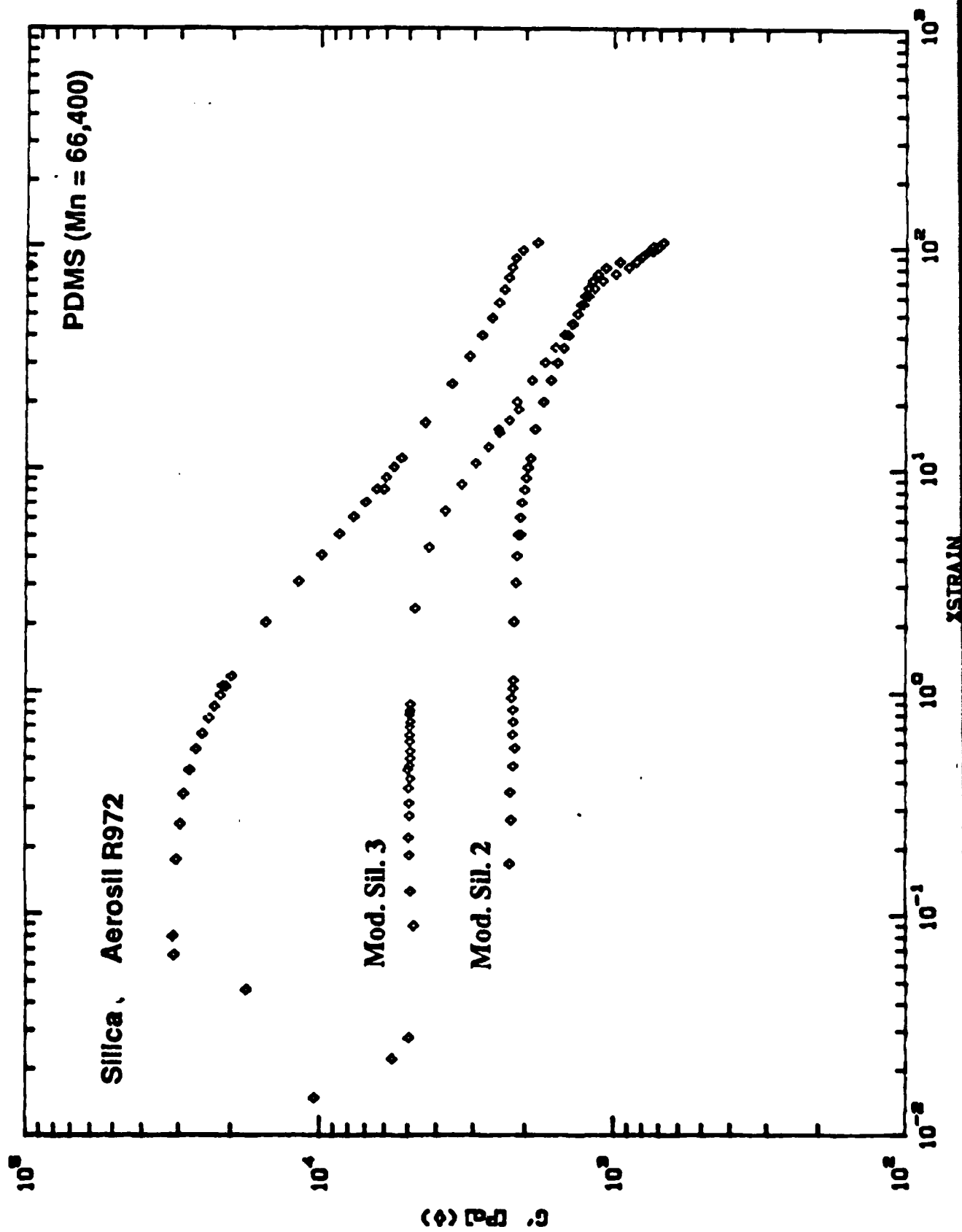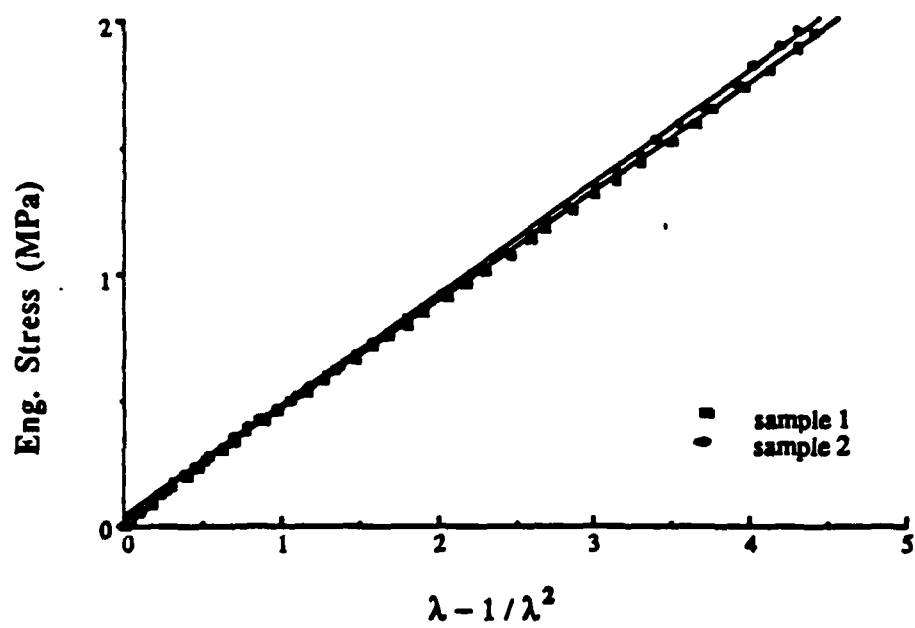Figure 8.

uncured rubber

cured rubber
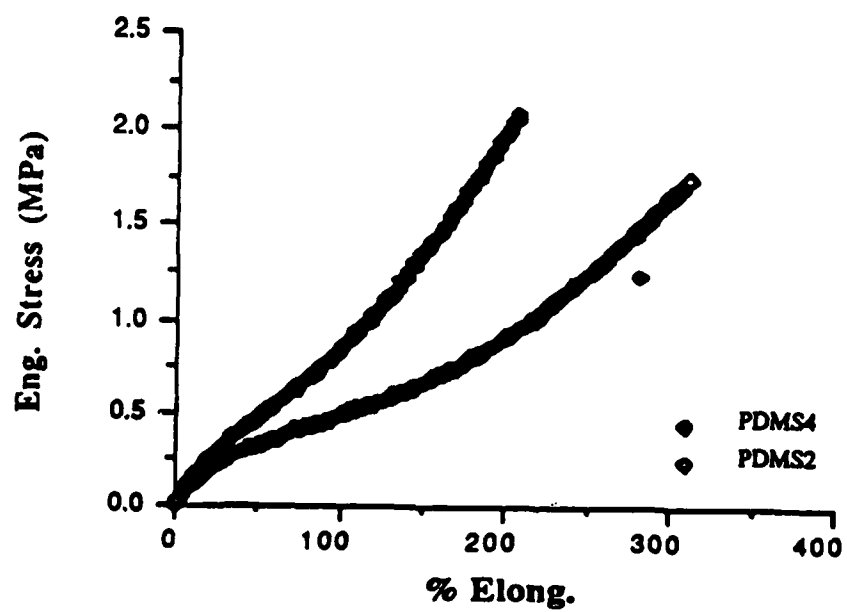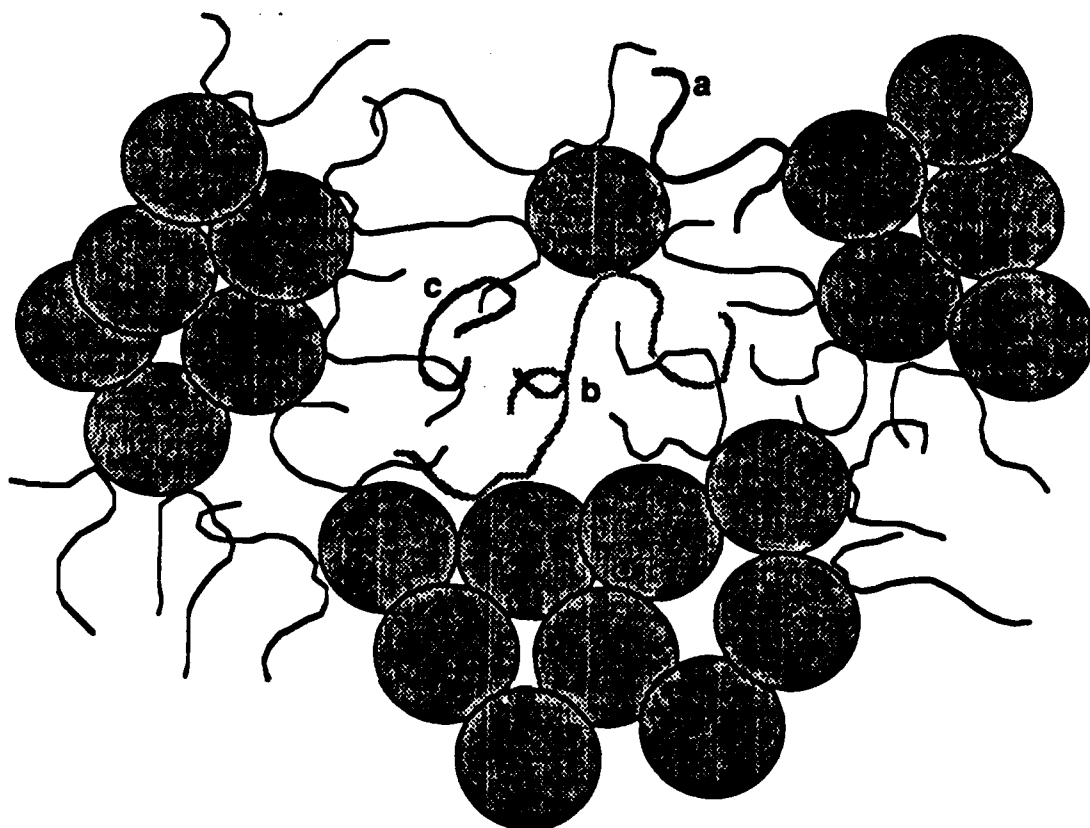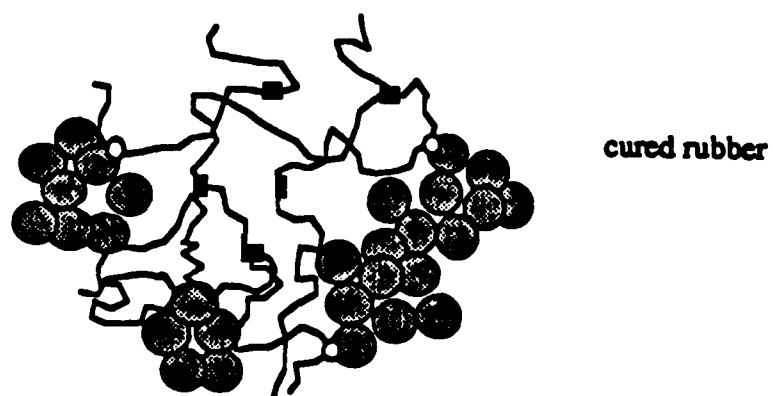
Figure 9

Figure 10

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